

AD-A186 378

18-NAPHTHALENE LINKED COFACIAL BINUCLEAR
PHTHALOCYANINES(U) YORK UNIV DOWNSVIEW (ONTARIO) DEPT
OF CHEMISTRY C C LEZNOFF ET AL. JUN 87 TR-16
A00148-84-G-8281

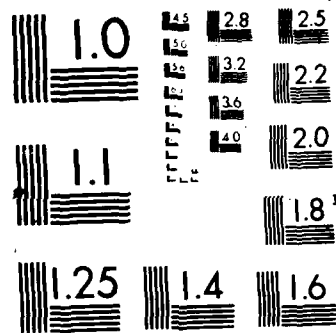
1/1

UNCLASSIFIED

F/G 7/3

NL





AD-A186 378

DTIC FILE COPY

12

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #16

DTIC
ELECTE
OCT 14 1987
S D

1,8-Naphthalene Linked Cofacial Binuclear Phthalocyanines

By

Prof. Clifford C. Leznoff, Herman Lam, Dr. Andrew Nevin,
Prof. Nagao Kobayashi, Dr. Pavel Janda and Prof. A.B.P. Lever

in

Angewandte Chemie

York University
Department of Chemistry
4700 Keele St., North York
Ontario, Canada M3J 1P3

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of the Document Control Data-DD form 1473. Copies of the form available from cognizant contract administrator

87 10 6 139

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified			3. DISTRIBUTION / AVAILABILITY OF REPORT As it appears on the report		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report # 16			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) 1,8-Naphthalene Linked Cofacial Binuclear Phthalocyanines					
12. PERSONAL AUTHOR(S) Leznoff, Clifford C.; Lam, Herman; Nevin, W. Andrew; Kobayashi, Nagao; Janda, Pavel; Lever, Alfred B.P.					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM Aug/86 TO Aug/87		14. DATE OF REPORT (Year, Month, Day) June 1987	
15. PAGE COUNT 13					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) phthalocyanine, electronic spectra, electrochemistry, spectroelectrochemistry, mixed valence species, cofacial phthalocyanine,		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Cofacial binuclear phthalocyanines linked by a three atom bridge are described, utilising the 1,8-position of the naphthalene nucleus. Electrochemical and uv/vis/nmr data are reported for the metal-free and cobalt derivatives in various oxidation states. Mixed valence cobalt species are discussed.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert K. Grasselli			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

DL/1113/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. R. Sutula
The Electrochemistry Branch
Naval Surface Weapons Center
Silver Spring, Maryland 20910

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auborn
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974

Dr. M. S. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, California 93555

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. Roger Belt
Litton Industries Inc.
Airtron Division
Morris Plains, NJ 07950

Dr. Ulrich Stimming
Department of Chemical Engineering
Columbia University
New York, NY 10027

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
Norwood, Massachusetts 02062

Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
~~York University~~
Downsview, Ontario M3J 1P3

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5H UNITED KINGDOM

Dr. John Wilkes
Department of the Air Force
United States Air Force Academy
Colorado Springs, Colorado 80840-6528

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Steven Greenbaum
Department of Physics and Astronomy
Hunter College
695 Park Avenue
New York, New York 10021

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. D. Rolison
Naval Research Laboratory
Code 6171
Washington, D.C. 20375-5000

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH UNITED KINGDOM

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Research Division
Mail Stop K 33/801
San Jose, California 95130-6099

Dr. Martha Greenblatt
Department of Chemistry, P.O. Box 939
Rutgers University
Piscataway, New Jersey 08855-0939

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymers Division
National Bureau of Standards
Gaithersburg, Maryland 20899

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402-5062

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531 Baltimore, Maryland 21218
S-751 21 Uppsala, Sweden

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT UNITED KINGDOM

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 68025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. Milos Novotny
Department of Chemistry
Indiana University
Bloomington, Indiana 47405

Dr. Mark A. McHugh
Department of Chemical Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

Dr. D. E. Irish
Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada
N2L 3G1

DL/1113/87/2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Henry S. White
Department of Chemical Engineering
and Materials Science
151 Amundson Hall
421 Washington Avenue, S.E.
Minneapolis, Minnesota 55455

Dr. Daniel A. Buttry
Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071

Dr. W. R. Fawcett
Department of Chemistry
University of California
Davis, California 95616

Dr. Peter M. Blonsky
Eveready Battery Company, Inc.
25225 Detroit Road, P.O. Box 45035
Westlake, Ohio 44145

ABSTRACTS DISTRIBUTION LIST, 051A

DL/1113/87/2

Dr. M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, California 90024

Dr. E. R. Bernstein
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80521

Dr. J. R. MacDonald
Chemistry Division
Naval Research Laboratory
Code 6110
Washington, D.C. 20375-5000

Dr. G. B. Schuster
Chemistry Department
University of Illinois
Urbana, Illinois 61801

Dr. J. B. Halpern
Department of Chemistry
Howard University
Washington, D.C. 20059

Dr. M. S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. W. E. Moerner
I.B.M. Corporation
Almaden Research Center
650 Harry Rd.
San Jose, California 95120-6099

Dr. A. B. P. Lever
Department of Chemistry
York University
Downsview, Ontario
CANADA M3J1P3

Dr. George E. Walrafen
Department of Chemistry
Howard University
Washington, D.C. 20059

Jr. Joe Brandelik
AFWAL/AADO-1
Wright Patterson AFB
Fairborn, Ohio 45433

Dr. Carmen Ortiz
Consejo Superior de
Investigaciones Cientificas
Serrano 121
Madrid 6, SPAIN

Dr. Kent R. Wilson
Chemistry Department
University of California
La Jolla, California 92093

Dr. G. A. Crosby
Chemistry Department
Washington State University
Pullman, Washington 99164

Dr. Theodore Pavlopoulos
NOSC
Code 521
San Diego, California 91232

Dr. John Cooper
Code 6173
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Joseph H. Boyer
Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148

Dr. Harry D. Gafney
Department of Chemistry
Queens College of CUNY
Flushing, New York 11367-0904



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Date	
A-7	

1,8-Naphthalene Linked Cofacial Binuclear Phthalocyanines*

By Prof.Clifford C.Leznoff, Herman Lam, Dr.W.Andrew Nevin, Prof.Nagao Kobayashi,[+] Dr.Pavel Janda[++] and Prof.A.B.P.Lever

Dept. of Chemistry
York University
4700 Keele St.,
North York (Toronto), Ont.,
Canada M3J 1P3

[+] Visiting Professor from the Pharmaceutical Institute, Tohoku University, Japan.

[++] Visiting research associate from the Heyrovsky Institute of the Czech Academy of Sciences, Prague, Czechoslovakia.

[#] This work was supported by grants from the Natural Sciences and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington). It was also partially funded by the Midwest Center for Mass Spectroscopy, of the National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8211164).

Binuclear phthalocyanines covalently linked by 5[1,2], 4[3], 2[3], 1[4] and -1[5] atom bridges have been recently described. We now report new cofacial binuclear phthalocyanines 1a-d linked by a 3 atom bridge on a rigid naphthalene framework. These compounds complement 1,8-anthracene bridged porphines[6,7], and provide entry to a new class of pillared phthalocyanines. They should prove of value in the photo- or electro-activation of small molecules, such as di-oxygen, carbon or sulphur dioxide.

Treatment of 4-iodophthalonitrile (2) (4.0g, 16mmol) and 1,8-diiodonaphthalene (3) (2.0g, 5.3mmol) in a mixed coupling reaction, in the presence of elementary nickel powder under conditions described for homocoupling reactions[8,9] led to 1,8-bis(3,4-dicyanophenyl)naphthalene (4) (310mg, 15.5% yield) as a mixture of syn and anti isomers due to restricted rotation about the 1,8-positions of the naphthalene nucleus (Scheme I). Conversion of 4 (380mg, 1mmol) into its isoindoline 5 and a mixed condensation of 5 with the isoindoline 6 prepared from 4-neopentoxypthalonitrile (6.0g, 28mmol) gave, following standard reaction conditions and chromatography[1-5] the desired 1,8-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)naphthalene (1a) in 15.5% yield. The di-cobalt, di-copper and di-zinc derivatives (1b-d) of 1a were prepared by refluxing 1a with CoCl₂, Cu(OAc)₂ and Zn(OAc)₂ respectively, as previously described.[1-5]

Scheme I Synthesis of 1,8-bis-2'-(9',16',23'-trineopentoxypthalocaninyl)-naphthalene 1a

The species 1a-d and 4 have been fully characterised.[10] The fast atom bombardment[11] (FAB) mass spectra of all the binuclear phthalocyanines 1a-d were most informative exhibiting parent ions as the base

peak in the high mass region above 500 AMU. Furthermore no evidence of partially or half-metallated derivatives of 1b-d were detected in their mass spectra. The ^1H nmr of 1a exhibited the upfield shifted NH protons which were absent in the zinc derivative 1d.

Electrochemical and spectroelectrochemical results show that the rigid geometry of the naphthalene bridge induces important changes in the cofacial dicobalt derivative 1b, compared with previously studied mononuclear and "clamshell" binuclear cobalt phthalocyanines.[1-4,12] The halves of the molecule of 1b do not oxidise and reduce at the same potential, resulting in clear splitting of the redox couples.

Cyclic and differential pulse voltammetry of 1b in o-dichlorobenzene (DCB) with 0.2 M tetrabutylammonium perchlorate as supporting electrolyte revealed a series of three oxidation and four reduction waves with halfwave potentials of +0.53, +0.14, 0.00, -0.90, -1.29, -1.68, and -2.08 V vs Fc^+/Fc . [13,14] Comparison with the cyclic voltammogram of the mononuclear parent compound, CoTNPC, ($E_{1/2}$ = +0.59, +0.03, -0.91, and -2.07 V in DCB[12]) indicates splitting of the first oxidation (L^+/L), and first reduction ($\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$) couples by 140 and 390 mV, respectively. This is the first example of clearly observed splitting of the redox waves in a ring bridged binuclear metal phthalocyanine and indicates a high degree of coupling between the halves of the molecule. Mixed valence L^+/L and $\text{Co}(\text{II})/\text{Co}(\text{I})$ species are thus potentially available.

In contrast to 1b, the splitting of the corresponding redox couple in the case of a so-called (-1) binuclear derivative (two phthalocyanine rings sharing a common benzene ring)[5] was less than 100mV (shoulder) in the mixed valence $\text{Co}^{\text{II}}-\text{Co}^{\text{I}}$ species. The reduction couples at -0.90 and -1.29 V were investigated by controlled potential

electrolysis in an optically transparent thin layer electrode (OTTLE) cell utilising a gold minigrid or platinum mesh working electrode. Stepwise reduction across each of the couples in turn gives the spectroscopic changes shown in Fig.1. Reduction over the first wave gives a green solution, with isosbestic points occurring at 322, 348, 545, 642, 664 and 760 nm (Fig.1(a)). The spectrum is unlike any seen previously for a reduced cobalt phthalocyanine, having a Q band at 650 nm. It does however exhibit a new absorption band in the region of 450-470 nm associated with metal-to-ligand charge transfer (MLCT) in the transition $\text{Co}^{\text{I}}\text{Pc}[\text{d}(\text{xz},\text{yz})] - \pi^*(1\text{b}_{1\text{u}})\text{Pc}$ of a $\text{Co}^{\text{I}}\text{Pc}$ species,[12,15,16] as well as a blue shift and increase in intensity of the Soret band.

The second reduction (Fig.1(b)) gives a yellow solution, with isosbestic points at 332, 395, 566, 678 and 758 nm. The final spectrum is very similar to that of the mononuclear $\text{Co}^{\text{I}}\text{TNPC}$ species,[12] indicating that both cobalt atoms have been reduced to Co^{I} . The spectra are fully reversible by stepwise oxidation to the initial species.

Nernstian plots of the spectroelectrochemical data over each of the reductions give slopes approaching 59 mV, showing that each step involves a one-electron transfer. Thus the product of the reduction at -0.90 V must be a mixed valence species 1e, of mainly $[\text{Co}^{\text{II}}-\text{Co}^{\text{I}}]$ character. The intensity of the MLCT band is only 35% of that of the fully reduced $[\text{Co}^{\text{I}}-\text{Co}^{\text{I}}]$ species, 1f spectrum, so that some delocalisation of the added electron over the phthalocyanine ring system may be occurring. The presence of the well resolved Q band at 650 nm, rather than ca. 710nm, may also indicate extensive delocalisation throughout the molecule. A weak absorption occurs in 1e, in the region of 800-900 nm (Fig. 1), absent from the spectra of both 1b and 1f and which may be an intervalence band.

The Q band region of the spectrum of 1e mixed valence species is very

different from that observed for the (-1) bridged mixed valence $[\text{Co}^{\text{II}}-\text{Co}^{\text{I}}]$ compound,[5] which has a split Q band at 700 and 760 nm.

Neither of the species 1b or 1f exhibit esr absorption in DCB. Species 1e, however, exhibits typical low spin $(d\pm 2)^1$ $\text{Co}(\text{II})$ esr absorption when 2-methylimidazole is added to the solution. The spectrum ($g = 2.25$) is very similar to that observed for the mixed valence $\text{Co}(\text{II})/\text{Co}(\text{III})$ species of a cofacial dicobalt porphyrin[17] Co_2FTF_4 , in the presence of N-methylimidazole.

In comparing these data with those for the corresponding cofacial binuclear dicobalt porphyrins[17-20] note that the latter also show splitting of the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ couple by up to 290 mV; however, unlike the phthalocyanines, no distinct changes in the electronic spectra were observed for the mixed valence species.[18]

Electrocatalytic reduction of oxygen was examined at electrodes (glassy carbon and ordinary pyrolytic graphite) covered with adsorbed 1b. Oxygen reduction occurred at -0.34 V vs SCE in cyclic voltammetric curves through pH 1 to pH 13, and the limiting current corresponding to two electron reduction of oxygen to hydrogen peroxide was observed in rotating disc experiments. Logarithmic analysis of the wave yielded a Tafel plot of -120 mV/decade, which corresponds to a charge-transfer coefficient of 0.5 and a one-electron transfer rate-determining step.

Figure 1. Development of the electronic spectra with time, showing the formation in DCB solution, of (a) the mixed valence $[\text{Co}^{\text{II}}-\text{Co}^{\text{I}}]$, 1e, and (b) the doubly reduced $[\text{Co}^{\text{I}}-\text{Co}^{\text{I}}]$, 1f obtained by reduction of 1b at potentials between -0.9 and -1.2V, and -1.3 and -1.6V vs Fc^+/Fc , respectively.

[1b] = $1 \times 10^{-4}\text{M}$, [TBAP] = 0.3M.

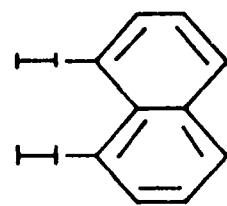
References

- [1] C. C. Leznoff, S. Greenberg, S. M. Marcuccio, P. C. Minor, P. Seymour, A. B. P. Lever and K. B. Tomer Inorg.Chim.Acta **89** (1984) L35.
- [2] C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever, K. B. Tomer Can.J.Chem. **63** (1985) 623.
- [3] C. C. Leznoff, S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever, K. B. Tomer Can.J.Chem. **63** (1985) 3057.
- [4] S. Greenberg, S. M. Marcuccio, C. C. Leznoff, K. B. Tomer Synthesis (1986) 406.
- [5] C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, A. B. P. Lever, J.Chem.Soc Chem.commun. (1987) 699.
- [6] C. K. Chang, H. Y. Liu, I. Abdalmuhdi J.Am.Chem.Soc. **106** (1984) 2725.
- [7] C. K. Chang, I. Abdalmuhdi J.Org.Chem. **48** (1983) 5388.
- [8] P. O. House, D. Kreopsell, W. Campbell, J.Org.Chem. **37** (1972) 1003.
- [9] H. Matsumoto, S. Inaba, R. Rieka J.Org.Chem. **48** (1983) 840.
- [10] The new compounds **4** and **1a-d** were completely characterised by the following physical and spectroscopic data. **4**: m.p. 285 °C; MS (EI): m/z 380(100%,M), 253(M-C₈H₃N₂); ¹H-nmr (300 MHz, DMSO-d₆); complex absorptions from δ = 7.3 - 8.5 analysed as a 1:1 mixture of syn and anti isomers; ir (KBr): ν = 3060, 2240 (CN), 1600, 1490, 835, 780 cm⁻¹; uv/vis (CH₂Cl₂): λ_{max} = 238 (ϵ = 21 900), 265 sh (ϵ = 17 000), 340 (ϵ = 11 000) nm, correct elemental analysis (C,H,N). - **1a**: MS(FAB): m/z 1670 (100%, M⁺, molecular ion cluster); ¹H nmr (300 MHz, CDCl₃): δ = -6.9, -6.1, -5.5 (br.wk.NH), 1.0-1.6 (br., 36H CH₃), 3.3-3.8 (br., 8H, OCH₂), 7.0 - 8.5 (br., aromatic); ir(KBr): ν = 3300(NH), 1615, 1245, 1100, 1020 (NH), 750 cm⁻¹;

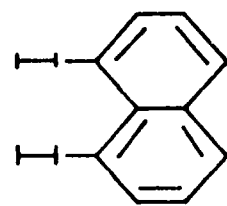
uv/vis (o-dichlorobenzene): $\lambda_{\max} = 340$ ($\epsilon = 79,500$), 648
 ($\epsilon = 77\ 600$) nm; correct elemental analysis (C,H,N). - 1b: MS(FAB)
 m/z 1784 (100%, $M^+ + 1$, molecular ion cluster); ir(KBr): $\nu = 2950$,
 1610, 1100, 740 cm^{-1} ; uv/vis (o-dichlorobenzene): $\lambda_{\max} = 306$ (ϵ
 = 141 000), 638 ($\epsilon = 123\ 000$), 674 ($\epsilon = 102\ 000$) nm. - 1c:
 MS(FAB): m/z 1793.6 (100%, $M^+ + 1$, molecular ion cluster); ir(KBr): ν
 = 2950, 1610, 1100, 740 cm^{-1} ; uv/vis (o-dichlorobenzene): $\lambda_{\max} =$
 300 ($\epsilon = 63,100$), 338 (102 000), 640 ($\epsilon = 95\ 500$), 686 ($\epsilon = 93\ 300$),
 - 1d: MS(FAB): m/z 1797.6 (100%, $M^+ + 1$, molecular ion cluster);
 ^1H nmr (300 MHz, CDCl_3): $\delta = 1.0 - 1.6$ (br., 36H, CH_3), 3.3-4.3 (br.,
 8H, OCH_2), 7.5 - 8.5 (br., aromatic); ir(KBr): $\nu = 2950$, 1610,
 1100, 740 cm^{-1} ; uv/vis (o-dichlorobenzene): $\lambda_{\max} = 298$ ($\epsilon = 72\ 400$),
 340 ($\epsilon = 112\ 000$), 640 ($\epsilon = 107\ 000$), 686 ($\epsilon = 93\ 300$) nm

- [11] M. Barber, R. S. Bordoli, R. D. Sedgwick, A. N. Tyler, J. Chem. Soc. Chem. Commun. (1981) 325.
- [12] W. A. Nevin, M. R. Hempstead, W. Liu, C. C. Leznoff, A. B. P. Lever Inorg. Chem. 26 (1987) 570.
- [13] R. R. Gagne, C. A. Koval, D. C. Lisensky Inorg. Chem. 19 (1980) 2854.
- [14] G. Gritzner, J. Kuta, Electrochim. Acta 29 (1984) 869.
- [15] M. J. Stillman, A. J. Thompson, J. Chem. Soc., Faraday Trans. 2, 70 (1974) 790
- [16] P. C. Minor, M. Gouterman, A. B. P. Lever, Inorg. Chem. 24 (1985) 1890.
- [17] Y. Le Mest, M. L'Her, J. Courtot-Coupez, J. P. Collman, E.R. Evitt, C.S. Bencosme J. Electroanal. Chem. 184 (1985) 331.
- [18] R. R. Durand Jr., C. S. Bencosme, J. P. Collman, F. C. Anson J. Am. Chem. Soc. 105 (1983) 2710.
- [19] J. P. Collman, M. Marrocco, C. M. Elliott, M. L'Her, J. Electroanal. Chem. 124 (1981) 113.
- [20] J. P. Collman, F. C. Anson, S. Bencosme, A. Chong, T. Collins, P.

Denisevich, E. Evitt, T. Geiger, J. A. Ibers, G. Jameson, Y. Konai, K. Meier, P. Oakley, R. B. Pettman, E. Schmittov, J. Sessler in B.M. Trost, C.R. Hutchinson, (Eds.) Organic Synthesis Today and Tomorrow, Pergamon Press, Oxford 1981.



+

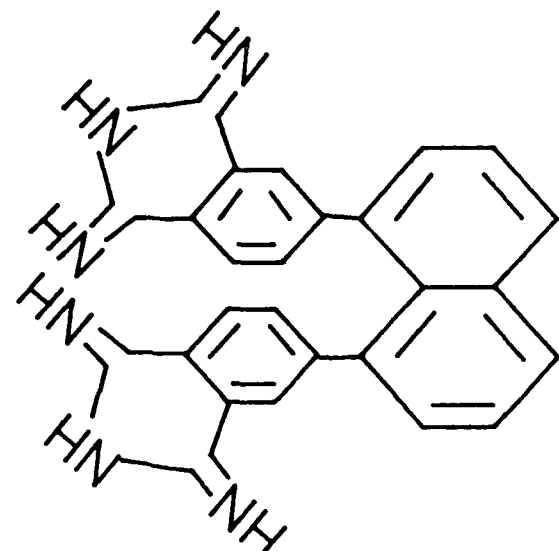


2

Ni(O)

DME 25 °C

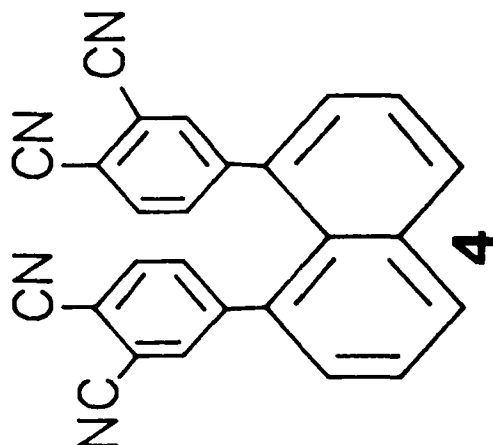
3



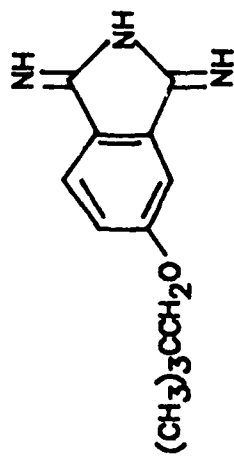
5

NH₃, NaOMe

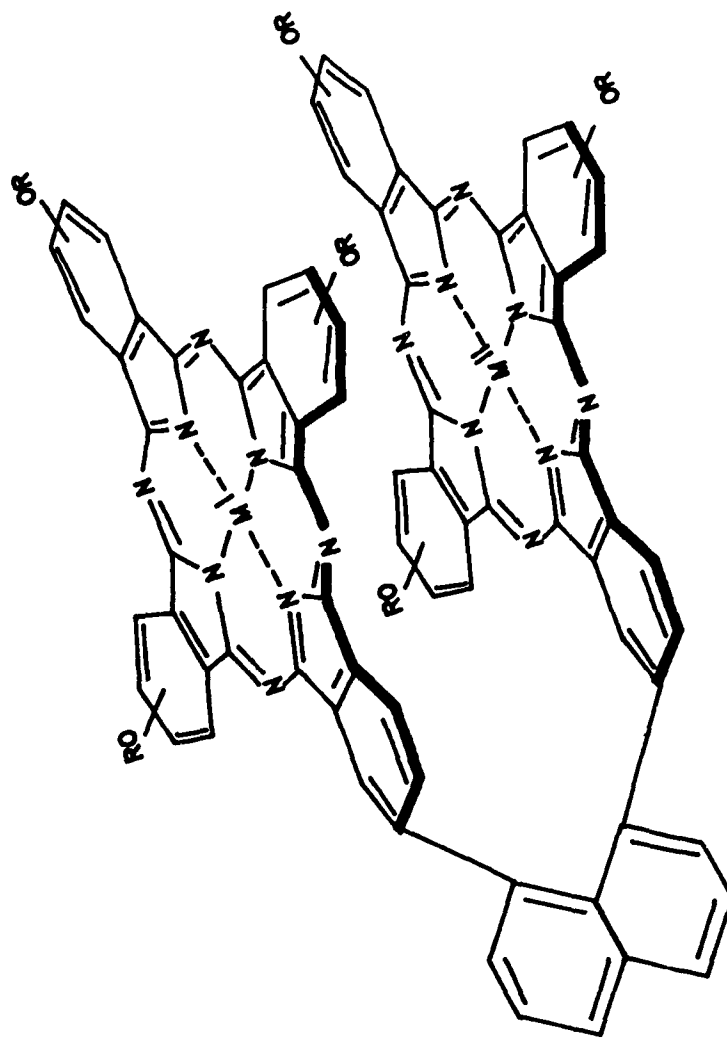
CH₃OH, 25 °C



4

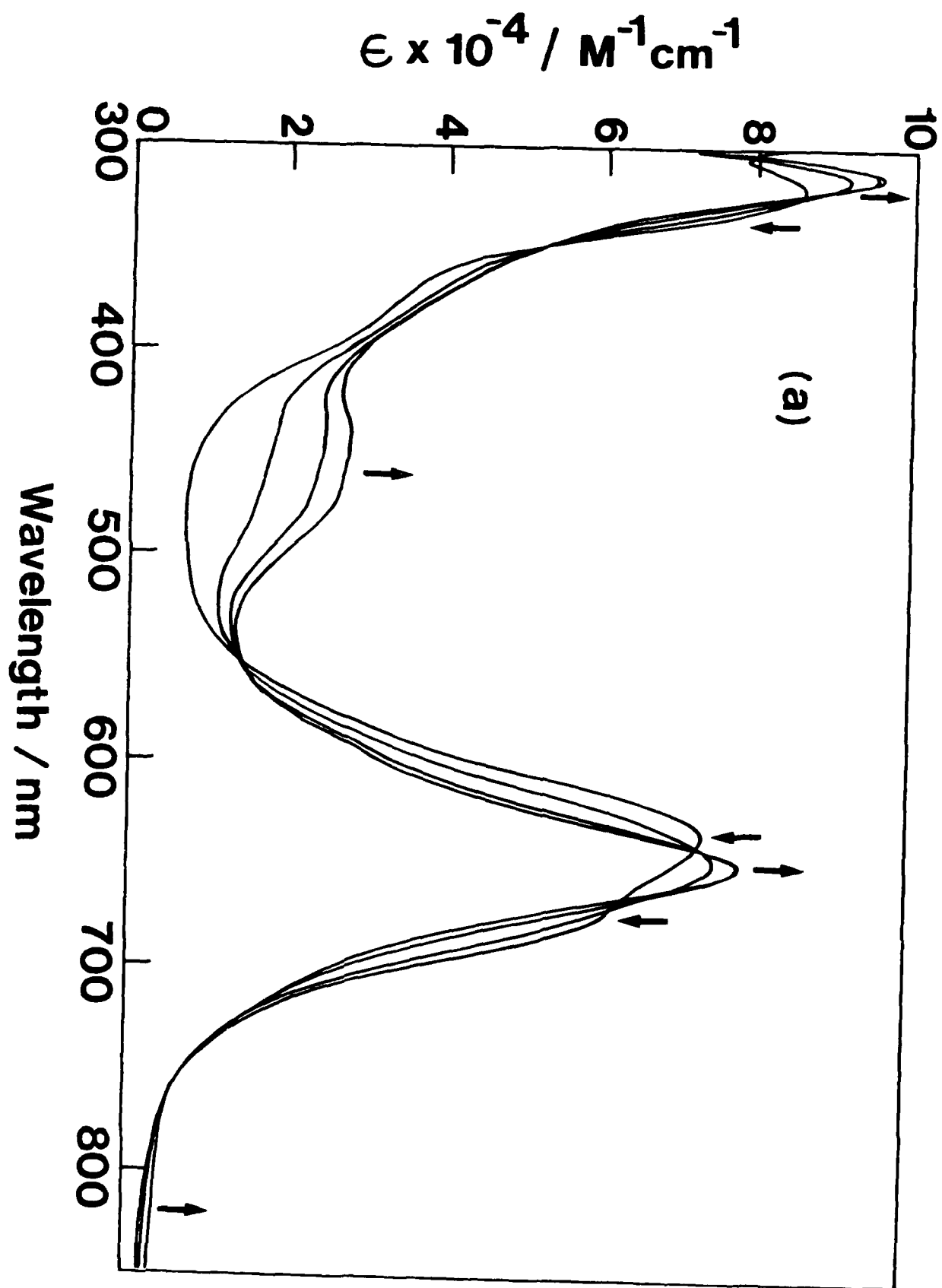


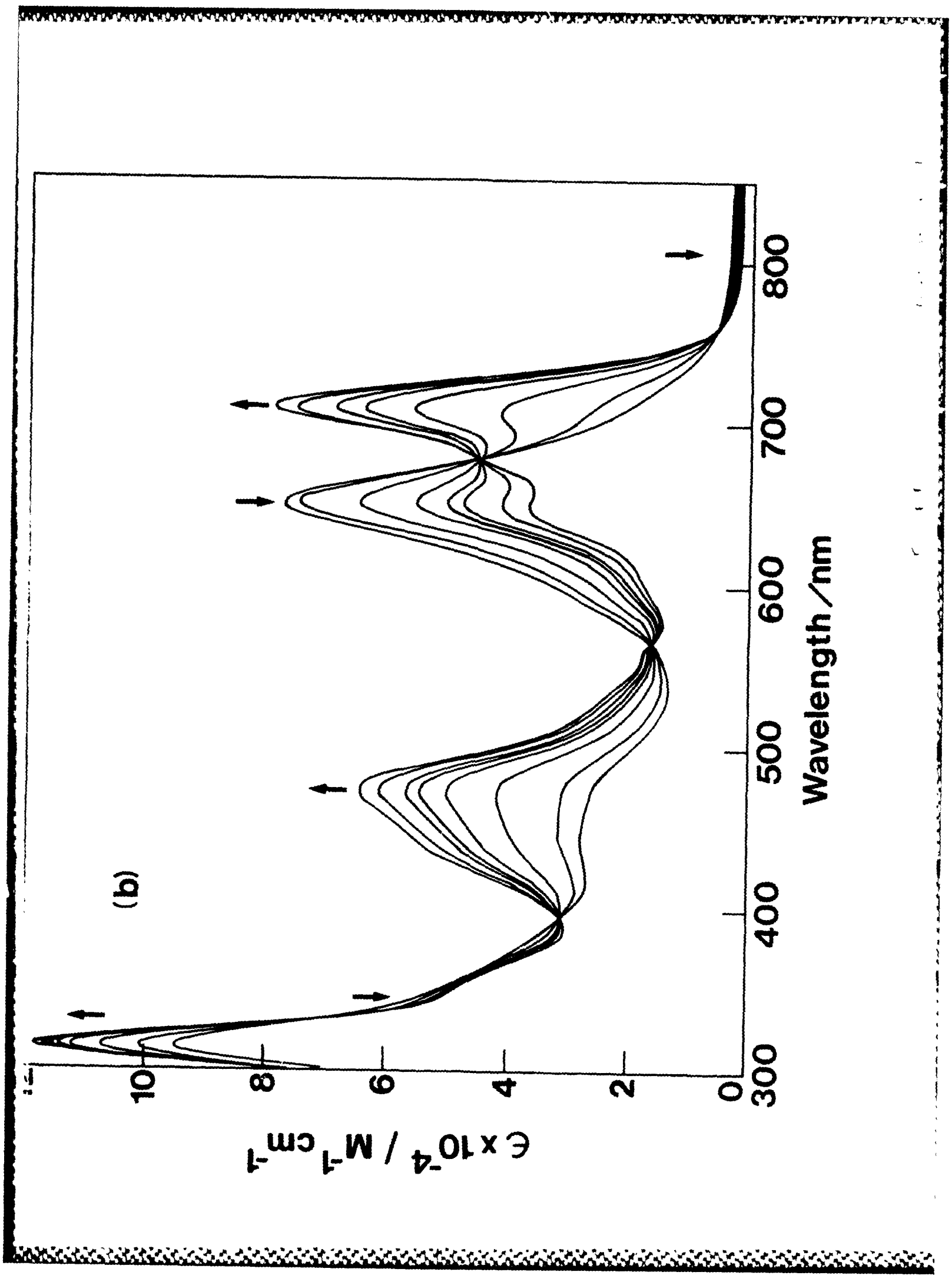
150°C, 72 h



- | | | | | | |
|----|-----|--|------------------|-------------------------------------|------------------|
| 1a | R = | CH ₂ C(CH ₃) ₃ | M ^I = | M ^{II} = | H ₂ |
| b | R = | CH ₂ C(CH ₃) ₃ | M ^I = | M ^{II} = | Co ^{II} |
| c | R = | CH ₂ C(CH ₃) ₃ | M ^I = | M ^{II} = | Cu ^{II} |
| d | R = | CH ₂ C(CH ₃) ₃ | M ^I = | M ^{II} = | Zn ^{II} |
| e | R = | CH ₂ C(CH ₃) ₃ | M ^I = | Co ^I , M ^{II} = | Co ^{II} |
| f | R = | CH ₂ C(CH ₃) ₃ | M ^I = | M ^{II} = | Co ^I |

Scheme 1





END

12-87

DTIC